CHAPTER 4

SAMARIA DOPED CERIA, ALUMINA AND SCANDIA DOPED ZIRCONIA - SYNTHESIS AND CHARACTERIZATION

4.1 INTRODUCTION

This chapter deals with the synthesis of bulk and thin films of 20 mol% Sm doped ceria as well as alumina scandia doped zirconia. For the case of bulk Sm doped ceria, characterization was done using XRD, SEM and AC Impedance Spectroscopy. Thin films of 20 mol% SDC was grown at different substrate temperature and oxygen partial pressures and films were characterized using XRD, SEM and AFM.

The reasons for choosing alumina in addition with scandia doped ZrO$_2$ is that, by adding alumina the sintering temperature can be reduced very much. Scandia was added in order to reduce the operating temperature of the zirconia system. The conductivity studies were carried out for both bulk and thin films of alumina and scandia doped zirconia.

4.2 EXPERIMENTAL

4.2.1 Synthesis of Bulk Samaria Doped Ceria

Glycine–nitrate process (GNP) (Ji et al 2003, Wang et al 2000), was used to synthesize foam-structured 20 mol% samaria doped ceria (SDC)
technique. Stoichiometric amounts (Mathews et al 2000) of Ce(NO$_3$)$_3$.H$_2$O (Aldrich, 99.99%) and Sm(NO$_3$)$_3$.xH$_2$O (Aldrich, 99.9%) were dissolved in distilled water, to which 0.5 mol glycine per mole nitrate was added. Combustion of the metal nitrate - glycine solution was performed in a glass beaker on a hotplate, with about 20 ml of the solution (0.1 mol with respect to metal ions) burned at a time. The precursor solution turned to a brown-red gel as solvent was evaporated and then spontaneous ignition occurred, leading to pale-yellow ash. The resultant ash was then collected and calcined in air at 873 K to remove any carbon residues remaining in the oxide powder.

4.2.2 Thin Film Preparation

Thin films of 20 mol% samaria-doped ceria, Ce$_{0.80}$Sm$_{0.20}$O$_{1.95}$ (SDC) were made from a sintered pellet of samaria doped ceria. All the films were deposited at different substrate temperature (473 - 973 K) and few experiments were also carried out by changing the oxygen partial pressure of 0.01mbar and 0.2mbar. After deposition, the chamber was cooled down to room temperature in the presence of oxygen (Na Ai et al 2006, Ji 2005, Perez-Coll et al 2003).

4.2.3 Synthesis of Bulk Alumina and Scandia Doped Zirconia

Samples were prepared, using a novel solution combustion technique. Appropriate amounts of zirconium nitrate (99.99%), scandium nitrate (99.99%) and aluminium nitrate (99.99%) were dissolved in distilled water. The solution is then saturated at 353 K over a hot plate. To the solution a saturated solution of urea is added as fuel and complexant (Kobayashi et al 2002, Anderson et al 1987). The amount of urea added was that required to consume completely the excess oxygen in the nitrate mixture and is called
stoichiometric amount. The resultant solution was then refluxed for 10 min. and introduced into an open muffle furnace maintained at 873 K. At this temperature excess water is removed from the solution resulting in the formation of a gel and its simultaneous combustion. The resulting fine powder was then calcined at 823 K for 30 min. The powder was then compacted to pellets of 15 mm diameter and sintered at 1873 K for 6 h. The sintered pellets were then used for pulsed laser deposition.

4.2.4 Thin Film Preparation

The thin films of alumina, scandia doped zirconia. The deposition of Al\textsubscript{2}O\textsubscript{3}-Sc\textsubscript{2}O\textsubscript{3} doped zirconium oxide thin films were carried out with a laser repetition rate of 10 Hz and energy density of 2 J/cm\textsuperscript{2} at the target. Sintered pellet of 0.88ZrO\textsubscript{2}-0.112Sc\textsubscript{2}O\textsubscript{3}-0.008Al\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} <001> of size 10 mm × 5 mm was used as target and substrate respectively. The deposition was performed at a pressure of 0.15 mbar for duration of 1 h.

4.3 RESULTS AND DISCUSSION

Figure 4.1 shows the XRD patterns of the as-synthesized ash, calcined SDC powder, and a sintered SDC pellet. The XRD pattern of the ash sample exhibits all major peaks of a fluorite structure, although the peaks are rather broad. However, all peaks in the XRD pattern of the powder samples calcined at temperatures above 600°C are relatively sharp, indicating that the Sm\textsubscript{2}O\textsubscript{3} has incorporated into the CeO\textsubscript{2} above 873 K form a solid solution with fluorite structure (Eguchi 1997).
Figure 4.1  X-ray diffraction patterns of the ash as synthesized by a glycine–nitrate process, the SDC powder calcined at 873 K, and a SDC pellet sintered at 1723 K.
4.3.1 Microstructure and Electrical Conductivity of Sintered SDC

The cross-sectional views of several sintered SDC pellets are shown in Figure 4.2. As expected, the grain size increased with sintering temperature, from about 0.5 μm at 1523 K, to 1 μm at 1623 K, and to 2 μm at 1450°C. The pore size and porosity also change with sintering temperature. However, the sintered densities of the pellet samples are larger than 92% of the theoretical value even at a sintering temperature as low as 1523 K. The relative densities increased to 95% and 97% when the sintering temperature was increased to 1623 K and 1673 K respectively (Eguchi 1992, Abrantes et al 2003).

Interpolated conductivity values at 500 and 600°C are tabulated in Table 5.1. It is well known that doped ceria behave as pure ionic conductors in air with negligible electronic conductivity. The conductivities increased slightly with sintering temperatures, implying that the grain boundary resistance does not make significant contribution to the total resistance, considering that the grain size increased about four times as the sintering temperature was increased from 1523 to 1673 K. The fact that the conductivities of samples sintered at 1523 K are comparable with those sintered at higher temperatures has significant implications. Lower sintering temperature may dramatically reduce the cost of fabrication.
Figure 4.2  SEM micrographs of the cross-sections of the SDC pellets sintered at 1523 K, 1623 K, and 1723 K for 5 h
Table 4.1  The conductivities at 773 K and 873 K of SDC pellet at different sintered temperatures

<table>
<thead>
<tr>
<th>Sintering temp (K)</th>
<th>Conductivity (773 K) S/cm</th>
<th>Conductivity (873 K) S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1523</td>
<td>0.00603</td>
<td>0.0129</td>
</tr>
<tr>
<td>1623</td>
<td>0.00620</td>
<td>0.0146</td>
</tr>
<tr>
<td>1723</td>
<td>0.00630</td>
<td>0.0167</td>
</tr>
</tbody>
</table>

4.3.2  Thin films of Samarium Doped Cerium Oxide

Figure 4.3 shows the XRD patterns of the 20mol% samarium doped ceria (SDC) thin films on (111) Si substrate, grown at $3.5 \times 10^{-5}$ mbar at various substrate temperature range from 303 to 973 K. The patterns clearly indicate polycrystalline nature of the films and the intensity of the peaks increase with increase in substrate temperature. It is evident from Figure that there are no lines corresponding to any impurity phases. The lattice parameter of the film changes with increasing substrate temperature as shown in Figure 4.4. There is a marked increase in the grain size with increasing temperature in accordance with an earlier observation in gadolinium doped ceria (Figure 4.5).
Figure 4.3 XRD pattern of SDC film at different substrate temperature on Si(111)
Figure 4.4  Lattice parameter as a function of substrate Temperature; SDC on Si(111)
Figure 4.5 FWHM and grain size as a function of substrate temperature on Si(111) at $3.5 \times 10^{-5}$ mbar.
4.3.3 Influence of oxygen partial pressure

Few experiments were also carried out by changing the oxygen partial pressure during deposition at 873K. Figure 4.6 illustrates the diffraction patterns obtained on the films deposited at 0.01 mbar and 0.2 mbar, respectively. It is evident from the figure that higher oxygen partial pressure aids in the improvement of the crystallinity of the samarium doped ceria. The increase in the crystallinity of the films at higher oxygen partial pressure is due to the increased incorporation of oxygen in the doped ceria lattice.

This is evident from the lattice parameter calculation. The lattice parameter of the film obtained at higher oxygen partial pressure matches very close to the lattice parameter of the bulk (0.542 nm).

Also we notice that the grain size decreases from ~34 nm to ~18 nm when the oxygen partial pressure increases from 0.01 mbar to 0.2 mbar. We have also studied the influence of oxygen partial pressure on the growth of SDC at a temperature 873K. Though the films are found to be polycrystalline in both the cases, there seems to be a change in the texture with change in the oxygen partial pressure. The intensity ratio \( I_{111}/I_{200} \) indicated increase in the ratio from 0.33 to 0.5 with increasing oxygen partial pressure.

The AFM images of the films grown at different oxygen partial pressure are shown in Figure 4.7. It is clear that the surface roughness increases with increasing oxygen partial pressure. The agglomeration of the grains is more pronounced at higher oxygen partial pressure.
Figure 4.6  XRD of SDC film at different O$_2$ partial pressure at 873 K on Si (111)
Figure 4.7  AFM images of 20 mol% SDC prepared at 0.1 and 0.2 mbar of oxygen partial pressure on Si (111)
4.4 ALUMINA AND SCANDIA DOPED ZIRCONIA

The most advanced SOFCs are those based on yttria-stabilized zirconia (YSZ) as the solid electrolyte operating around 1173 K. Although there are advantages to high temperature operation, it does place severe constraints on material selection and on the lifetime of the fuel cell. Lowering the operating temperature to 873 K, would permit use of oxidation-resistant metallic alloys as the interconnect material; it would also enhance the reliability and life of the cell, minimize the electrode/electrolyte interactions, permit more frequent cycling and reduce the operating cost. This can be achieved by using dense pore free thin films of material having superior oxide ion conductivity to that of YSZ, as the solid electrolyte. The two most promising materials are Sr and Mg doped LaGaO$_3$, La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-(x+y)/2}$ (LSGM) and alumina and scandia doped zirconia. Thin dense pore free films of LSGM of various compositions were synthesized (Mathews et al 2000, Wakabayashi 1988) using pulsed laser deposition (PLD) and electrophoretic deposition (EPD). There are no reports on the synthesis of alumina and scandia doped zirconia thin films by PLD. Here we report the synthesis of Al$_2$O$_3$ and Sc$_2$O$_3$ doped ZrO$_2$ through soft chemistry route and fabrication of thin films by pulsed laser ablation.

The compound 0.88 ZrO$_2$-0.12 Sc$_2$O$_3$ has a rhombohedral structure at room temperature and undergoes transformation to cubic fluorite structure around 923 K. The cubic phase can be stabilized down to room temperature by substituting a small portion of Sc$^{3+}$ with Al$^{3+}$. For the compositions synthesized in this study the crystal structure obtained is cubic. The XRD pattern corresponding to the composition 0.88ZrO$_2$-0.112Sc$_2$O$_3$-0.008 Al$_2$O$_3$ is shown in Figure 4.8. Similar patterns were obtained for all the compositions (x = 0.006, 0.007, 0.008). The ionic radii of Sc$^{3+}$ and Zr$^{4+}$ are
Figure 4.8 Powder XRD pattern of $0.88\text{ZrO}_2 - 0.112\text{Sc}_2\text{O}_3 - 0.008\text{Al}_2\text{O}_3$ (Al$_2$O$_3$-Sc$_2$O$_3$ doped zirconia) bulk sintered target material
almost similar, therefore in the same co-ordination; the entropy gain on randomization of the cations (configurational entropy) is relatively small.

When the ions are of different size, in the same co-ordination, the configurational entropy is greater and hence more driving force for randomization. Since the difference in ionic radii of Al$^{3+}$ and Zr$^{4+}$ is greater than that of Sc$^{3+}$ and Zr$^{4+}$ (Sc$^{3+}$ and Zr$^{4+}$ have similar ionic radii), the introduction of small amount of Al$^{3+}$ into the cation sublattice increases the configurational entropy. This additional configurational entropy is the extra driving force for randomization and decreases the number of micro-domains (crystallite seeds) of the low temperature rhombohedral phase.

For the various compositions synthesized in the study, assuming that the thermo chemical reaction occurs with the stoichiometric quantity of the fuel, the balanced combustion reaction can be written as

$$0.88\text{Zr(NO}_3\text{)}_4 \text{(aq)} + 2(0.12-x)\text{Sc(NO}_3\text{)}_3 \text{(aq)} + 2x\text{Al(NO}_3\text{)}_3 \text{(aq)} + 3.55\text{CO(NH}_2\text{)}_2 \text{(aq)}$$

$$\rightarrow 0.88\text{ZrO}_2-(0.12-x)\text{Sc}_2\text{O}_3-x\text{Al}_2\text{O}_3 + 7.1 \text{H}_2\text{O} + 3.55\text{CO}_2 + 5.672\text{N}_2$$  \hspace{1cm} (5.1)

The product of rapid combustion has resulted in very fine powders due to the large amount of gases evolved during reaction (5.1). About 16 moles of gases are evolved for each mole of stabilized zirconia. The low processing temperature required for the formation of the cubic phase when the material is synthesized via the solution route is because of the effective homogeneous mixing (randomization) of cations, in atomic level, achieved in a liquid solution. Formation of metal-urea complex and its ignition take place simultaneously so that the random distribution of cations achieved in the solution is retained until ignition. Moreover, although the furnace temperature
is kept below 873 K, the particle attains temperature in excess of 1273 K during combustion. This is inferred from the color of the flame (colorless in this case).

Powders obtained by combustion as well as after high temperature (1873 K) sintering and cooling at 5°/min rate were found to be of cubic crystal structure upon XRD analysis.

4.4.1 Thin Film Fabrication

XRD patterns of thin films deposited at substrate temperatures of 873 and 1023 K at an ambient oxygen pressure of 0.15 mbar on Al₂O₃ (001) are shown in Figure 4.9. The AFM pictures, both two and three dimensional of the thin films grown on sapphire substrate are shown in Figure 4.10. It is clear from the AFM pictures that the films are dense and free of pores. The thickness of the films measured using Dektak-3010 surface profilometer was found to be ~ 1.0 microns.

Though the films were grown at temperature where the rhombohedral phase is stable, a cubic phase was obtained as evidenced by XRD studies. This is because of Al₂O₃ doping as well as the complete random distribution of ions, atoms and molecules in the vapour and plasma phases formed during the ablation and their extremely rapid condensation at a substrate followed by nucleation and growth.
Figure 4.9 XRD pattern of thin films of $0.88\text{ZrO}_2\cdot0.112\text{Sc}_2\text{O}_3\cdot0.008\text{Al}_2\text{O}_3$ prepared at 873 and 1023 K on (001) $\text{Al}_2\text{O}_3$ of 0.15mbar pure oxygen
Figure 4.10  The 2D and 3D AFM images of thin films prepared at different substrate temperatures (a), (b) 873 K and (c), (d) 1023 K.
4.4.2 Bulk and Thin Film Conductivity

The cole-cole plot obtained for the bulk samples at 1073 K is given in Figure 4.11. The contribution due to grain boundary is clearly visible. The bulk conductivity values obtained from the AC impedance study at various temperatures are given in Figure 4.12. The corresponding values for YSZ obtained from literature (Inaba and Tagawa 1996, Wakabayashi and Yamamoto 1988) are also shown for comparison.

The cole-cole plot obtained for the thin films at 1073 K is shown in Figure 4.13. The contribution from grain boundary is not clearly visible as in comparison to that of the bulk. This is because in the bulk sample there is segregation of Al$_2$O$_3$ at the grain boundaries above an Al$_2$O$_3$ concentration of 0.006 (Bastow et al 2004), which is not detected by XRD, where as in thin films samples obtained by PLD the solubility of Al$_2$O$_3$ will be greater than that of bulk samples because of the vapour and plasma phases formation prior to condensation and growth of the film. The conductivity values for the thin films are given in Figure 4.14. The conductivity values are higher for the thin films compared to that of bulk.
Figure 4.11 Typical complex impedance cole-cole plot between imaginary impedance ($Z''$) and real impedance ($Z'$) of $\text{Al}_2\text{O}_3$-$\text{Sc}_2\text{O}_3$ doped zirconia pellet measured at 1073 K.
Figure 4.12 Arrhenius plots of electrical conductivities of $\text{Al}_2\text{O}_3$-$\text{Sc}_2\text{O}_3$ doped zirconia and reported conductivity value of YSZ
Figure 4.13  Typical complex impedance cole-cole plot between imaginary impedance ($Z''$) and real impedance ($Z'$) of Al$_2$O$_3$-Sc$_2$O$_3$ doped zirconia thin films on (001) Al$_2$O$_3$ substrates deposited at 873 K and 0.15 mbar pure oxygen, conductivity measured at 1073 K
Figure 4.14  Arrhenius plots for electrical conductivities of Al₂O₃-Sc₂O₃ doped zirconia thin films prepared on (001) Al₂O₃ at 873 K and 0.15 mbar pure oxygen. Bulk values are shown for comparison.
4.5 SUMMARY AND CONCLUSIONS

The chapter deals with the synthesis of Sm doped ceria bulk and thin films, and alumina Scandia doped zirconia and their characterization. These two systems were synthesized by combustion technique. These materials are expected to reduce the sintering temperature. The XRD result of the calcinated Sm doped ceria showed that the peaks are sharp at above 873 K of calcinations temperature. The thin films of Sm doped ceria were grown and characterized for various properties. From the AFM images of the films grown at different oxygen partial pressure it is clear that the surface roughness increases with increasing oxygen partial pressure. The agglomeration of the grains is more pronounced at higher oxygen partial pressure.

The conductivity studies were carried out for both bulk and thin films of alumina and scandia doped zirconia. Results showed that the conductivity is higher for the thin films compared to that of bulk. This is because in bulk sample there is segregation of Al₂O₃ at the grain boundaries above an Al₂O₃ concentration of 0.006, which is not detected by XRD, where as in thin films samples obtained by PLD such segregation was not observed.